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## PATENT SPECIFICATION

### 587,273



Convention Date (United States of America): Oct. 17, 1942.

Application Date, (In United Kingdom): Nov. 5, 1943. No. 18368/43.

Complete Specification Accepted: April 21, 1947.

### COMPLETE SPECIFICATION

#### Improvements in or relating to Diesel Fuel Compositions

The present invention are those in which the metal constituent is attached to the aromatic some other negative such as sulfur.

### ERRATA

SPECIFICATION No. 587,273.

Page 4, line 24, for "P" read "Y"  
Page 4, line 83, for "corresponding" read "corresponding"

THE PATENT OFFICE,  
22nd November, 1949.

N.P

- tion of the fuel  
incomplete combustion or  
severity of the combustion conditions.
- 25 technical and economical reasons the fuels used in Diesel engines are usually petroleum gas oil fractions, whose boiling ranges are somewhat higher than those of kerosene, for instance, about 375° F. to 650° F. Under certain conditions of operation these gas oil fuels tend to form carbonaceous and resinous residues. Such residue formation is obviously disadvantageous in that it interferes with the normal running of the engine and reduces its efficiency. For example, deposits may build up on the valves to such an extent that the valves will stick and result in erratic operation of the engine.
- 30 40 In accordance with the present invention, certain metal derivatives of organic compounds have been found to be very effective for accomplishing the object of reducing combustion chamber deposits in Diesel engines when mixed in small amounts with the Diesel fuel.

The preferred metal derivatives used in the present invention comprise metal salts of aromatic hydroxy compounds, particularly those salts which contain a metal constituent linked to an aromatic nucleus through oxygen. Analogous compounds suitable for use in the present

of the and preferably pounds have the type formula  $M(ZAr)_n(S)_x$ , wherein Z represents, generically, a negative radical or atom.

The characteristic formula may have a number of modifications, for example, the aromatic radical may be mono- or poly-cyclic; the number, kind, and position of alkyl substituents in any of the aromatic nuclei may be varied; also, other substituent groups, e.g., amino groups, alkoxy groups, or elements such as halogen or phosphorus may be introduced either in the aromatic ring or the alkyl side chains.

Examples of phenol side compounds which may be employed in accordance with the present invention include barium di-isobutyl phenol sulfide (barium iso-octyl phenol sulfide), barium di-isobutyl phenol disulfide, calcium di-tertiary amyl phenol sulfide, cobalt hexyl phenol sulfide, magnesium cetyl phenol disulfide, and barium octadecyl cresol sulfide. Metal phenolate salts which may be used include calcium di-isobutyl phenolate, barium salts of petroleum phenols, magnesium tertiary amyl phenolate, barium salt of cashew

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### COMPLETE SPECIFICATION

#### Improvements in or relating to Diesel Fuel Compositions

We, STANDARD OIL DEVELOPMENT COMPANY, a corporation duly organised and existing under the laws of the State of Delaware, United States of America, having an office at Linden, New Jersey, United States of America, do hereby declare the nature of this invention, and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

This invention relates to the utilization of an agent which checks fouling of a Diesel engine by combustion chamber deposits.

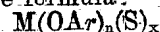
Compression-ignition engines classified as Diesel engines are characterized by liquid fuel injection and auto ignition of the fuel. These engines present certain fouling problems in the nature of varnish-like deposits on the pistons and contamination of the lubricating oil which arise from incomplete combustion of the fuel and severity of the combustion conditions. For technical and economical reasons the fuels used in Diesel engines are usually petroleum gas oil fractions, whose boiling ranges are somewhat higher than those of kerosene, for instance, about 375° F. to 650° F. Under certain conditions of operation these gas oil fuels tend to form carbonaceous and resinous residues. Such residue formation is obviously disadvantageous in that it interferes with the normal running of the engine and reduces its efficiency. For example, deposits may build up on the valves to such an extent that the valves will stick and result in erratic operation of the engine.

In accordance with the present invention, certain metal derivatives of organic compounds have been found to be very effective for accomplishing the object of reducing combustion chamber deposits in Diesel engines when mixed in small amounts with the Diesel fuel.

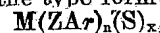
The preferred metal derivatives used in the present invention comprise metal salts of aromatic hydroxy compounds, particularly those salts which contain a metal constituent linked to an aromatic nucleus through oxygen. Analogous compounds suitable for use in the present

invention are those in which the metal constituent is attached to the aromatic nucleus through some other negative radical or negative atom, such as sulfur. Also, in general, it is preferred to have the aromatic nucleus or aryl radical in the compound contain one or more alkyl side chain substituents, e.g., propyl, isopropyl, butyl, isobutyl, tertiary butyl, amyl, isoamyl, di-isobutyl (iso-octyl) cetyl, octadecyl, or analogous aliphatic radicals in order to obtain the desired degree of solubility in the Diesel fuel being employed.

A particularly preferred group of metal salts belonging to the class above described comprises salts of hydroxy-aromatic sulfides which may be represented by the following type formula:



wherein Ar represents aliphatic substituted aromatic nuclei; M is the metal constituent linked thereto through oxygen, n is an integer corresponding to the valence of the metal M; and x is an integer, 1 to 4, and preferably 1 or 2. Analogous compounds have the type formula



wherein Z represents, generically, a negative radical or atom.

The characteristic formula may have a number of modifications, for example, the aromatic radical may be mono- or poly-cyclic; the number, kind, and position of alkyl substituents in any of the aromatic nuclei may be varied; also, other substituent groups, e.g., amino groups, alkoxy groups, or elements such as halogen or phosphorus may be introduced either in the aromatic ring or the alkyl side chains.

Examples of phenol side compounds which may be employed in accordance with the present invention include barium di-isobutyl phenol sulfide (barium iso-octyl phenol sulfide), barium di-isobutyl phenol disulfide, calcium di-tertiary amyl phenol sulfide, cobalt hexyl phenol sulfide, magnesium cetyl phenol disulfide, and barium octadecyl cresol sulfide. Metal phenolate salts which may be used include calcium di-isobutyl phenolate, barium salts of petroleum phenols, magnesium tertiary amyl phenolate, barium salt of cashew

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nut shell phenol (cardanol), calcium cetyl phenolate, and calcium octadecyl phenolate.

Instead of the metal salts of aromatic sulfides and metal phenolates described above, one may use metal derivatives of other hydroxy compounds, such as alcohols, enolates, salicylates, and the like. All of these above-described compounds can be classed generically under the general formula  $MXY$ , in which  $M$  represents a metal,  $X$  represents oxygen or a member of the sulfur family, and  $Y$  represents an organic radical such as aryl or alkyl or the radical of a corresponding thioether, di-sulfide, or other derivative thereof as explained above. In all of these compounds the metal is attached through  $X$  to a carbon atom in the organic radical  $Y$ , which latter carbon atom in turn is connected only to carbon or hydrogen.

Although the present invention is primarily concerned with addition agents of the general formula  $MXY$ , as described above, other metal compounds may be used in conjunction with these such as metal derivatives of organic-substituted inorganic acids, such as phosphoric and phosphorous acids and thio derivatives as well as sulfonates. For instance, calcium octadecyl phosphate or barium octyl monothiophosphite may be used as well as the calcium or barium salt of a di-substituted thiophosphoric acid, prepared by reacting cetyl phenol with  $P_2S_5$ . Examples of sulfonates include the calcium salt of oil-soluble mahogany sulfonic acids, derived by treating a petroleum oil fraction with fuming sulfuric acid, and calcium tri-isobutyl phenol sulfonate.

The phenolate compounds considered particularly useful for the present purposes may be described as being salts derived preferably from alkylated phenols, such as are obtained from various natural sources, or synthetically by reacting phenol with an alkylating agent, such as an olefin. Suitable phenols, then, include petroleum phenols and phenolic materials from cashew nut shells or other vegetable sources, as well as phenol, cresol, naphthol, etc. which has been alkylated with olefins or alcohols of sufficient molecular weight to impart adequate solubility to the finished metal salts. Also, preferably, the alkyl phenols contain a negative substituent group, such as sulfur, in a thioether linkage or disulfide linkage. These are readily obtained by reacting an alkylated phenol compound with sulfur monochloride, sulfur dichloride, or a mixture of the two chlorides.

A particularly useful additive can thus

be prepared by alkylating phenol with di-isobutylene (the dimer of isobutylene) under suitable conditions to give di-isobutyl phenol (also called iso-octyl phenol or tetramethyl butyl phenol). This alkylated phenol is then caused to react with sulfur monochloride or dichloride to form the di-isobutyl phenol monosulfide or disulfide which is then converted to the desired metal salt by reaction with a metal oxide or hydroxide. An advantageous method of preparation of these additives is described in U.S. Patent 2,294,145 of Winning, VanVoorhies, and McNab. The desired alkylated phenol or phenol sulfide is added to a vehicle such as a mineral oil and then neutralized with a suitable basic acting metal compound, preferably in the presence of a small amount of a higher alcohol such as stearyl alcohol which acts as a foam-suppressing agent and is finally filtered. The product is a concentrate of the desired additive in mineral oil. This concentrate may be advantageously used in the present invention as a convenient means of introducing the additive into the Diesel fuel. In addition, the presence of a small amount of lubricating oil in the fuel will prevent the separation of normally solid metal derivatives in manifolds or other parts of the engine when the fuel is vaporized.

The metal to be substituted for hydrogen in the hydroxyl group of the phenols for obtaining the desired agents may be selected from metals of the alkali metal group, alkaline earth metal group, aluminium, chromium, tin, iron, nickel, cobalt, and related metals, but the preferred metal is one of the alkaline earth metal group which forms a soft, substantially non-abrasive ash on burning, e.g., barium, calcium, magnesium, etc., barium being especially preferred.

Metallic additives especially preferred for this invention are barium di-isobutyl phenol sulfide, barium di-isobutyl phenol disulfide, and calcium octadecyl phenolate.

Very small amounts of the effective metal derivatives are sufficient to realize a substantial improvement in the Diesel engine condition. These agents may be used in a proportion of from about 0.01% to 1.0% by weight of the Diesel fuel oil for a substantial improvement even though these compounds have little or no effect on the ignition quality or other properties of the fuel.

The above-described metal derivatives may be used in conjunction with other additives which are capable of enhancing their effectiveness. High molecular weight aliphatic alcohols, such as stearyl

alcohol, are particularly useful in this respect. Also, phenolic ethers, such as the tertiary butyl ether of ortho tertiary butyl *p*-cresol, may be similarly employed.

Although it is not intended that the invention be limited thereby, the following example is given to illustrate the distinctively beneficial results obtained in applying the present invention to the operation of a full scale single cylinder Caterpillar Diesel engine under normal operating conditions for a run of 120 hours.

#### EXAMPLE.

Employing the method described by Winning, VanVoorhies and McNab in U.S. Patent 2,294,145, a 50% additive concentrate was prepared from di-isobutyl phenol sulfide (iso-octyl phenol sulfide), di-isobutyl phenol disulfide (iso-octyl phenol disulfide), stearyl alcohol and barium hydroxide octahydrate, Ba(OH)<sub>2</sub> · 8H<sub>2</sub>O. The final product contained 20% barium di-isobutyl phenol sulfide, 20% barium di-isobutyl phenol disulfide, 10% stearyl alcohol and 50% of mineral lubricating oil which was an extracted Mid-Continent oil of about 52 seconds Saybolt viscosity at 210° F. Two Diesel engine tests were then made, one with this additive in the fuel and one

without it, as a control test for comparison. The fuel used in both tests was a refined hydrocarbon Diesel fuel having an A.P.I. gravity of about 36.5, a cetane number of about 51, an initial boiling point of about 410° F., and a final boiling point of about 640° F. For the test representing this invention the fuel was blended with 0.12% of the mineral oil additive concentrate prepared as just described above, the total material added comprising, on the weight of fuel, 0.06% mineral oil, 0.012% stearyl alcohol, 0.024% barium di-isobutyl phenol sulfide, and 0.024% di-isobutyl phenol disulfide. In both runs the engine was lubricated with a conventionally refined Coastal naphthenic lubricating oil of about 55 Saybolt seconds viscosity at 210° F.

After each run the engine parts were inspected and given demerit ratings based on their condition. The individual ratings were weighted according to their relative importance and an overall rating calculated from them. It should be noted that the lower the demerit rating, the better the engine condition and hence the better the performance of the fuel in the engine with respect to absence of deleterious deposits. The results of these engine tests are recorded in the following table:

TABLE.

120-Hour "Caterpillar Diesel Engine Tests" under Normal Operating Conditions, 16.7 BHP, 850 RPM, 160° F. Oil Temperature, 180° F. Water Jacket Temperature.

Test No.	Operation	Engine Demerits			
		Overall	Ring Zone	Heat Groove	Oil Filter
1	With fuel only	0.95	1.19	5.50	3.00
2	With fuel containing metal phenolate sulfide additive	0.75	0.80	3.50	1.75

It will be readily seen that after test 2 in which the compounded fuel of this invention was used, the engine parts were much cleaner than after test 1 employing the non-compounded fuel. It should be particularly noted that the additive not only improved the areas with which the fuel combustion product would normally tend to come into contact but also affected the crankcase lubricant as denoted by the lower demerit rating for the oil filter.

Further improvements in engine cleanliness can be effected by employing additives of the types herein described in both the Diesel fuel and the crankcase lubricant and it is intended that the present

invention should include operation of Diesel engines in this manner. This is particularly advantageous when the Diesel engine is to operate under severe heavy duty service.

The phenolate agents may be used incorporated in the fuel or both agent and fuel may be supplied to the engine separately to mix before combustion during the operation, whenever needed, as when the engine is running under heavy load or toward the end of the operation.

The metallic additives of this invention may also be used in the same fuel with other Diesel fuel additives such as anti-oxidants or ignition promoters.

It is not intended that this invention be limited to the specific examples given for the purpose of illustration.

Our prior British Specification No. 551,852 describes an improved oxidation resisting composition comprising a hydrocarbon such as lubricating oil or natural or synthetic rubber having compounded therewith a polyvalent metal salt of a dihydroxy dialkyl diaryl sulfide or polysulfide or polymer, or tellurium or selenium analogue thereof, at least one of the valencies of the metal being connected to an alkoxy group.

Having now particularly described and ascertained the nature of our said invention, and in what manner the same is to be performed, we declare that what we claim is:—

1. A Diesel fuel containing a small amount of a compound having the general formula  $MX.Y$ , in which M is a metal, X is oxygen or a member of the sulfur family and P is an organic radical, the metal M being attached through X to a carbon atom in the organic radical Y, which latter carbon atom is in turn connected only to carbon or hydrogen.

2. A Diesel fuel containing a major proportion of hydrocarbon Diesel fuel base stock and a small amount of a metal aroxy compound adapted to reduce the formation of deleterious residues by the fuel in a Diesel engine.

3. A Diesel fuel comprising a major proportion of hydrocarbon Diesel fuel base stock boiling below the lubricating oil boiling range, and a small amount of an alkaline earth metal salt of an alkylated hydroxy aromatic sulfide.

4. A Diesel fuel containing a small amount of a compound having the general formula  $M(OAr)_n(S)_x$ , wherein Ar represents aliphatic - substituted aromatic nuclei, M is a metal constituent linked thereto through oxygen,  $n$  is an integer corresponding to the valence of the metal M, and  $x$  is an integer, 1 to 4.

5. A Diesel fuel containing from about

0.01% to 1% of a metal phenolate sulfide for reducing the carbon residue formation by the fuel in a Diesel engine.

6. A Diesel fuel comprising a major proportion of a gas oil Diesel fuel fraction and a small amount of a metal derivative of an alkylated phenol sulfide containing a total of at least 10 aliphatic carbon atoms.

7. A Diesel fuel containing a major proportion of a hydrocarbon Diesel fuel base stock and about 0.01% to 1% of barium di-isobutyl (iso-octyl) phenol sulfide.

8. A Diesel fuel comprising a major proportion of a hydrocarbon Diesel fuel base stock and a small amount of a mixture of a metal alkyl phenol sulfide and a metal alkyl phenol disulfide.

9. A Diesel fuel comprising a major proportion of a hydrocarbon Diesel fuel base stock and a small amount of a mixture of barium di-isobutyl phenol sulfide and barium di-isobutyl phenol disulfide.

10. The method of reducing deleterious deposits in the combustion zone of a Diesel engine comprising supplying to said combustion zone during the operation of said Diesel engine a Diesel fuel containing a small amount of a metal derivative of a compound selected from the class of organic hydroxy compounds and the corresponding thio compounds, the Diesel fuel and the additive being supplied to the engine separately.

11. The method of operating a Diesel engine comprising supplying to its combustion zone during operation a Diesel fuel containing a small amount of a metal aroxy compound, and simultaneously lubricating said Diesel engine with a crankcase lubricating oil containing a small amount of a metal aroxy compound.

Dated this 5th day of November, 1943.

D. YOUNG & CO.,  
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London, W.C.2.

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